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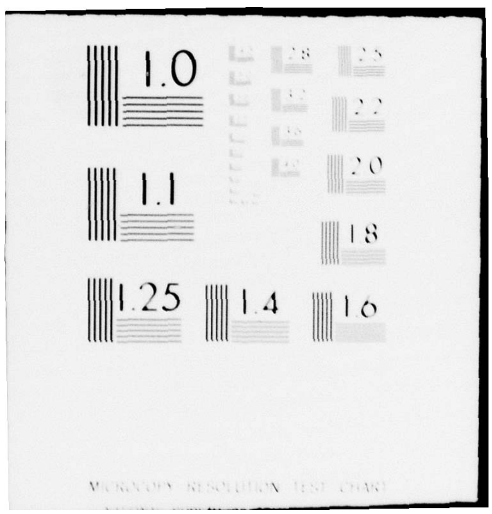
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NRL Memorandum Report 3888

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# The Electronic and Electro-Optic Future of III-V Semiconductor Compounds


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An assessment of material development of III–V compounds for electro-optic, microwave and millimeter wave technology is presented. Questions concerning material selection, needs and processing is addressed.

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## CONTENTS

# THE ELECTRONIC AND ELECTRO—OPTIC FUTURE OF III—V SEMICONDUCTOR COMPOUNDS

## Introduction

This report will present the rationale for the extensive materials efforts being expended by the DoD in III-V materials. The background and the current status will be summarized, however, there are a number of extensive review articles and conference proceedings available for this information (1,2,3,).

Questions concerning the materials properties, electro-optic physics, chemical properties and device potential will be presented to help resolve the more fundamental questions: why work on the III-V materials which are inherently more costly than silicon? and, do the III-V alloys have any advantage over other semiconductors? In order to fully evaluate these alloys the potential of the materials for devices must be discussed. At the outset, it must be stated that the major effort in the microwave and millimeter wave properties of the III-V alloys is being funded by the Department of Defense; however, in the fiber optic communication area there is considerable commercial potential and private industry is supporting a significant effort.

## Microwave and Millimeter Wave Materials

The motivating drives within the semiconductor device industry are higher efficiency, speed and power and lower cost, noise and size. The development of silicon for solid state electronics resulted in a major change in communications, computations, and other technologies. Indeed, today it is difficult to find an area of modern civilization untouched by the silicon revolution. Certainly the military has undergone an evolution in its basic strategy due in no small measure to the electronic capability available with silicon based semiconducting devices.

This change in the electronic capability has occurred in less than 30 years with the introduction of, initially, the silicon transistor and then the integrated circuit. Silicon was not the first semiconducting material in spite of its overwhelming dominance. Initially, transistors were, and are still to a limited extent, made from germanium. However the energy gap of germanium, 0.65 eV, is too low, and intrinsic conduction occurs below $100^{\circ}C$ thus limiting the operating characteristics of germanium semiconducting devices.

Note: Manuscript submitted October 5, 1978.

Silicon has an energy gap of 1.11 eV and intrinsic conduction does not occur below 250°C; thus the useful operating range of silicon devices is improved compared to germanium. Other advantages of silicon are seen in Table I where in terms of utilization the ability for a diffusion based technology was and is a prime consideration for integrated circuit devices and systems. It is not necessary to point out the impact the silicon integrated circuit has made on the military system applications as devices as automotive ignition systems to advanced missiles and satellites. The silicon integrated circuit has made significant changes in the everyday life styles of each person in the civilized world from toys to modern communications.

Indeed, if one considers the tremendous range of current and potential applications of silicon in electronics it is quite logical to ask: why spend large amounts of resources to develop other semiconductor material technologies which do not have many of the obvious advantages of silicon. Among the disadvantages of the III-V compounds: they are relatively difficult to prepare, the elements are quite costly, they do not appear suitable for a diffusion based technology, and, at least to date, they are difficult to passify.

These disadvantages notwithstanding, in the area of microwave and millimeter wave technology the devices based on III-V materials can perform functions which cannot be readily achieved using silicon. As seen in Table II the band gaps of GaAs and InP are higher than silicon; therefore higher operating temperatures are possible. At the charge carrier velocities, necessary for high speed operation, gallium arsenide (GaAs) and indium phosphide have distinct advantages over silicon. Figure 1 shows that the low field mobility of GaAs (8600 $cm^2$/v-sec) is greater than InP (4000 $cm^2$/v-sec) which in turn is significantly greater than Si; at higher fields the velocity of the carriers in InP is significantly higher than in the others which projects a higher frequency of operation for devices based on InP. It is also evident that in contrast with Si, InP and GaAs possess a region of negative differential mobility which is used to advantage in transferred electron devices, TED. Already microwave tubes are being displaced by the III-V semiconductors for low power applications. Today, 5W devices at 8 GHz

have been prepared (4) and there are projections for 5W devices at 20 GHz (5). Higher speed computers will require devices based on the III-V technology since silicon, even with submicron technology, is velocity limited. Signal processing in the millimeter or microwave range frequencies requires devices and material properties not available in silicon. NRL is currently doing in-house III-V material preparation activity in bulk single crystals and both liquid epitaxial growth in thin single crystals and device research for microwave and millimeter wave devices. Other DoD laboratories having significant in-house microwave materials and devices efforts include Naval Ocean Systems Center, Air Force Wright Patterson AFSC, and the Army laboratories in the Electronics Command.

## Fiber Optics

While the present primary commercial application of fiber optics is as either decorative or functional light guides, it has long been recognized that the enormous commercial potential of fiber optics lies in its use for short and long range communications. Recent advances in fiber optics component technology have paved the way for moving optical communications systems out of the laboratory and into commercial use. This fact was dramatically demonstrated in the summer of 1977 when both the Bell System (in its Chicago experiment) and ITT (at a location north of London) announced that they were installing commercial telephone service over optical links.

The advantages enjoyed by fiber optics systems compared to their conventional coaxial cable or twisted wire communications systems counterparts are shown in Table III.

All of these advantages are reflected in urgent Naval and Air Force Communications Systems requirements for point-to-point, distributive network, and intrusion resistant and radiation hardened systems.

The basic building blocks of a fiber optic data transmission system are: 1) a transmitter (a solid state light source), 2) a transmission path (an optical fiber), and 3) a receiver (a solid state detector). The major technical breakthrough in long distance data transmission occurred in 1970 when Corning Glass Works announced the development of low loss, high quality fused silica fibers.

These fibers had attenuation losses as low as 20 dB/Km. Since then, fiber attenuation has dropped steadily. Presently, attenuations of 0.5 dB/Km or less have been achieved in the 1.1 to 1.3 μm region.

An optimum light source is one which can couple maximum power with adequate bandwidth into the optical fiber. Its wavelength should suffer only minimum attenuation in the fiber and should match the maximum responsivity of the photodetector. Materials selection for such solid state light sources reduces very rapidly to the III-V materials. The indirect band gap of the elemental semiconductors and the stoichiometric variations of II-VI materials eliminate these two classes of materials from consideration. If, when we consider the III-V materials, we eliminate from consideration those compounds formed with B or N (since the preparation of these materials is difficult and insufficiently advanced to make P-N junction devices practical), then nine binary compounds and their 18 ternary alloys remain. Figure 2 shows: 1) six of these binary compounds and the distinct wavelengths they provide and 2) several of the more widely investigated ternary alloys and the wavelength ranges to which they correspond.

The most widely used fiber optics light sources are LED or laser structures based on the GaAs-AlGaAs system. This system yields the most efficient room temperature LEDs and CW lasers, because even without close control of alloy composition, this alloy system can provide almost perfectly lattice matched heterojunction optoelectronic devices over the entire alloy compositional range. The lattice matching inherent in this system effectively eliminates the misfit dislocations common at heterojunction interfaces of other alloy systems with poor lattice fit. The presence of such dislocations causes minority carrier recombination, morphology and surface recombination problems which degrade or prevent device operation.

The function of the receiver or solid state light detector in a fiber optic system is to convert light signals to electrons which can be handled by traditional circuitry. For the 0.8 to 0.9 wavelength range of the GaAs-AlGaAs emitters, silicon avalanche or P-I-N photodiodes are the most commonly used detectors because of their high efficiency, low noise, uniform response and high reliability.

For long range optical communications one disadvantage of GaAs-AlGaAs sources is that their 0.8 to 0.9 μm output is not optimally matched to the characteristics of the best available optical fibers. State-of-the-art fused silica fibers exhibit minimum absorption and dispersion in the 1.1 to 1.3 μm region. To take advantage of this inherent property of low loss fibers, so crucial to the successful solution of pressing Naval and Air Force long range optical communications problems, several in-house laboratories are actively engaged in the development of III-V quaternary alloy systems. Quaternary alloys have one more degree of freedom than ternary alloys. This additional degree of freedom permits the independent variation of the energy bandgap and the lattice constant over wide ranges. Of the possible quaternary alloy systems covering this wavelength range the GaInAsP-InP system appears to be the most promising because:

(1) Well controlled thin films have been grown via LPE; (2) Room temperature DH lasers emitting at wavelengths between 1.0 and 1.3 μm have been fabricated successfully; (3) Operating lifetimes in excess of 5000 hours have been achieved. Thus it appears, that the necessary exploratory research for adequate source development in this alloy system is well underway. Rome Air Development Command is doing growth of bulk InP single crystals and vapor phase epitaxial growth of binary and quaternary alloys. Other DoD laboratories are doing vapor phase and liquid phase growth of III-V compounds for electro-optic applications.

## Current Efforts and Results

The in-house activities on III-V materials at the Naval Research Laboratory and at Rome Air Development Command, L. G. Hanscom Field were undertaken to meet some of the critical needs for better substrates of GaAs and InP as well as to prepare epitaxial layers for electronic and electro-optic applications. The programs were so divided that semi-insulating substrates and liquid phase epitaxial growth of GaAs and InP was performed at NRL and "n" and "p" substrates of InP and vapor phase epitaxial growth of GaAs was performed at RADC. Samples and information exchange were performed between the two laboratories as well as with other laboratories working in the III-V area.

It was found quite early that the commercially available compounded InP and GaAs was not of sufficient purity to prepare reproducible substrate material. A compounding apparatus developed by E. Swiggard, et al (6) that uses a pyrolytic boron nitride (PBN) boat and protective liners (Fig. 3) has resulted in the ability to prepare high purity GaAs and InP with no detectable Si impurities. The impurity level of the GaAs is so low the material becomes semi-insulating due to residual oxygen.

The high purity GaAs and InP is grown in single crystal form using the liquid encapsulated Czochralski method (Fig. 4) and a PBN crucible to hold the melt (7). Typical properties of the grown single crystals are shown in Table IV. The GaAs can be prepared in semi-insulating form with residual oxygen doping for ion implantation applications and Cr/Te doped for liquid and vapor phase epitaxial growth. The semi-insulating InP is Fe doped with the dopant concentration an order of magnitude lower than that previously necessary. The single crystals have been used in in-house laboratories and in industry for physical and device evaluation; and results to date are so promising that industry is adopting the methods developed. A manufacturing technology program is scheduled for funding this fiscal year. GaAs FETs have been prepared by direct ion implantation into the non-intentionally doped substrate. Results to date indicate state-of-the-art device performance with potentially major cost savings. The ability to prepare GaAs and InP devices by ion implantation directly into the substrate holds the promise of eliminating a major disadvantage of the III-Vs when compared to Si, namely III-V technology could be a diffusion like technology.

For the first time InP FETs have been prepared by ion implantation (8) as a result of the availability of high purity semi-insulating InP substrates. InP MISFETs have also been prepared and may open the potential of an MOS technology for the III-Vs.

The liquid phase epitaxial growth is performed in an apparatus shown in Fig. 5. The introduction of a second well in the sliding seal boat has allowed the growth substrates to be etched just prior to growth. The etch back removes any damaged layer which may develop by heating and processing before growth (10). The epitaxial layers grown in this manner have resulted in the ability to make GaAs microwave devices having no extra buffer

layers to protect the active layer from the substrate. V.L. Wrick, et al (11) have used the etch back process to grow epitaxial InP layers of extremely high purity which previously was not attainable. The processes developed are being used to prepare both microwave and electro-optic devices and can result in significant savings by having better epitaxial layer uniformity and reproducibility as well as by reducing the cost and increasing yield by removing the extra step of growing a buffer layer.

As already mentioned for long range fiber optics communication systems, available quartz fibers show minimum absorption and dispersion in the 1.1 to 1.3 micron range and InP-GaInAsP sources are developing nicely. Detector development, however, has not proceeded as smoothly. GaInAsP-InP photodetectors have been developed which have demonstrated greater responsiviity at 1.05 μm than the best Si photodiodes operating at 0.85 μm. However development of quaternary avalanche and P-I-N diodes has not proceeded quite as smoothly due to the higher purity requirements necessary for efficient operation. LPE systems have thus far not successfully demonstrated the ability to reduce the as grown carrier concentrations to much below $1 \times 10^{16}$ carriers/$cm^3$ without resorting to prolonged baking cycles.

In the case of GaAs, VPE systems have been used very successfully to achieve high purity layers ever since the mole fraction effect was first described by Cairns and Fairman (12). Clarke (13) in England and Fairman, et al (14) in the U.S.A. have successfully shown that the mole fraction effect can also be used to prepare very high purity InP. In order to successfully fabricate high efficiency detector structures for the 1.1 to 1.3 μm range by VPE, a vapor phase system must be developed which can successfully deposit high purity GaInAsP. The hydride system originally described by Tiejten and Armick (15) appears to be ideally suited to handle the growth of GaInAsP when modified as shown in Fig. 9. Kennedy, et al (16,17) have successfully shown that the mole fraction effect also applied to the hydride system (Fig. 6) and have also determined the effect of the Ga/As ratio (Fig. 6), deposition temperature (Fig. 7), and HCl concentration (Fig. 8) on mobility of the deposited GaAs layers. A double tube hydride system designed to study the effect of various growth parameters on the purity of GaInAsP layers is currently under construction at RADC/ES (Fig. 9).

## Conclusion

The promise of the III-V technology for military applications is just beginning to be realized. Those areas of electronics which can use the inherent cost advantages of silicon will continue to do so. However, use of the III-Vs will result in the development of new technologies in high speed logic and data processing, in compact and reliable microwave and millimeter wave systems, and in a revolutionary use of electro-optics for communications and control functions. An example of the potential of the electro-optics is that in the first year of full service of a fiber optic link in Chicago by Bell Telephone an average outage rate of 0.02% or less for a conventional trunking system went down to a projected rate of 0.0001% for the optical link. Projected lifetimes for III-V lasers at room temperature are over one million hours.

Thus, the cooperative in-house materials efforts are and will continue to aid the development of these new technologies in areas where the prime user is the military. Future work will be done in these military laboratories having the unique capabilities for materials development. Already significant advances have taken place in programs at NRL and RADC on a cooperative basis and industry is voluntarily making tests and devices using the in-house materials.

## Acknowledgements

The work reported on is a summary of the activities of a number of scientists at the Naval Research Laboratory and Rome Air Development Command including E. Swiggard, R. Henry, S. Lee, P. Nordquist, W. Potter, and D. Davies.

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Table I

Advantages of Semiconducting Silicon

1. Elemental semiconductor.
2. Relative ease to purify and grow single crystal.
3. Diffusion based technology.
4. Native oxide passification.
5. Inexpensive and plentiful element.
6. Large base in commercial technology.

Table II

Physical Properties of Si, GaAs and InP

| | Si | GaAs | InP |
| --- | --- | --- | --- |
| Molecular weight | 28.06 | 144.64 | 145.79 |
| Density (gm/cc) | 2.328 | 5.316 | 4.787 |
| Themo cond (w/cm$^{o}$C) | 1.41 | 0.54 | 0.68 |
| Melting point ($^{o}$C) | 1415 | 1,238 | 1.070 |
| Mobility (cm$^{2}$/v-sec) (300$^{o}$C) | 1900 | 8,600 | 4,000 |
| Eg (eV) | 1.11 I | 1.43D | 1.35D |

Table III

Advantages of Fiber Optics Systems over Traditional Communications Systems

- Increased immunity to EMI and EMP.
- Dielectric isolation between transmitter and receiver.
- For greater intrusion resistance and security.
- Wide signal bandwidths.
- No spark, fire or short circuit hazards.
- Smaller, lighter, and lower loss cables.
- Ultimately lower cost.

Table IV

Properties of LEC Grown GaAs and InP Crystals

| Material | Dopant | Mobility ($cm^2$/v-sec) | Resistivity (ohm-cm) | Etch Pit Density $cm^{-2}$ |
|---|---|---|---|---|
| GaAs | residual $O_2$ | 4000 (RT) | $10^8$ | $1\text{-}5 \times 10^3$ |
| GaAs | Cr:Te | 1200 (RT) | $10^8$ | $1\text{-}5 \times 10^3$ |
| InP | - | 25,000 ($77^o$) | - | $1\text{-}5 \times 10^4$ |
| InP | Cr | - | $10^{3-4}$ | $1\text{-}5 \times 10^4$ |
| InP | Fe | - | $10^7$ | $1\text{-}5 \times 10^4$ |

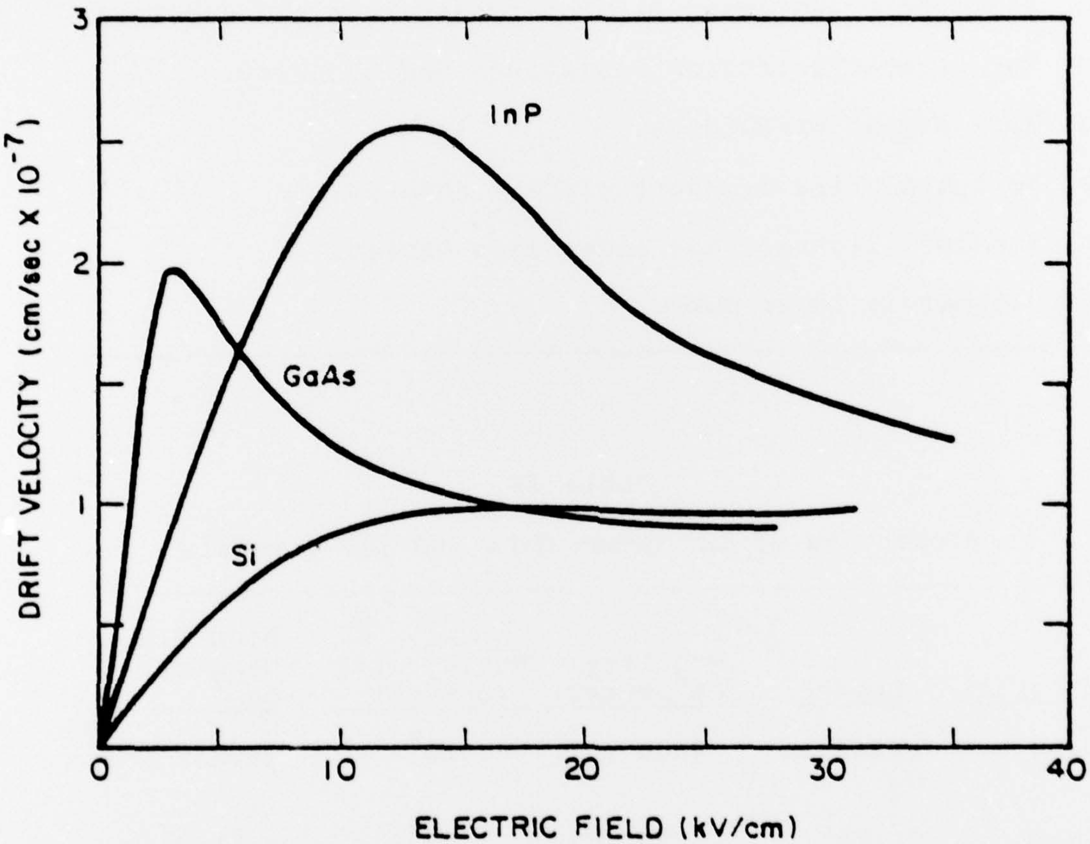



Fig. 1 — Drift velocity versus electric field for GaAs, Si and InP

## III — V TERNARY ALLOYS (18)

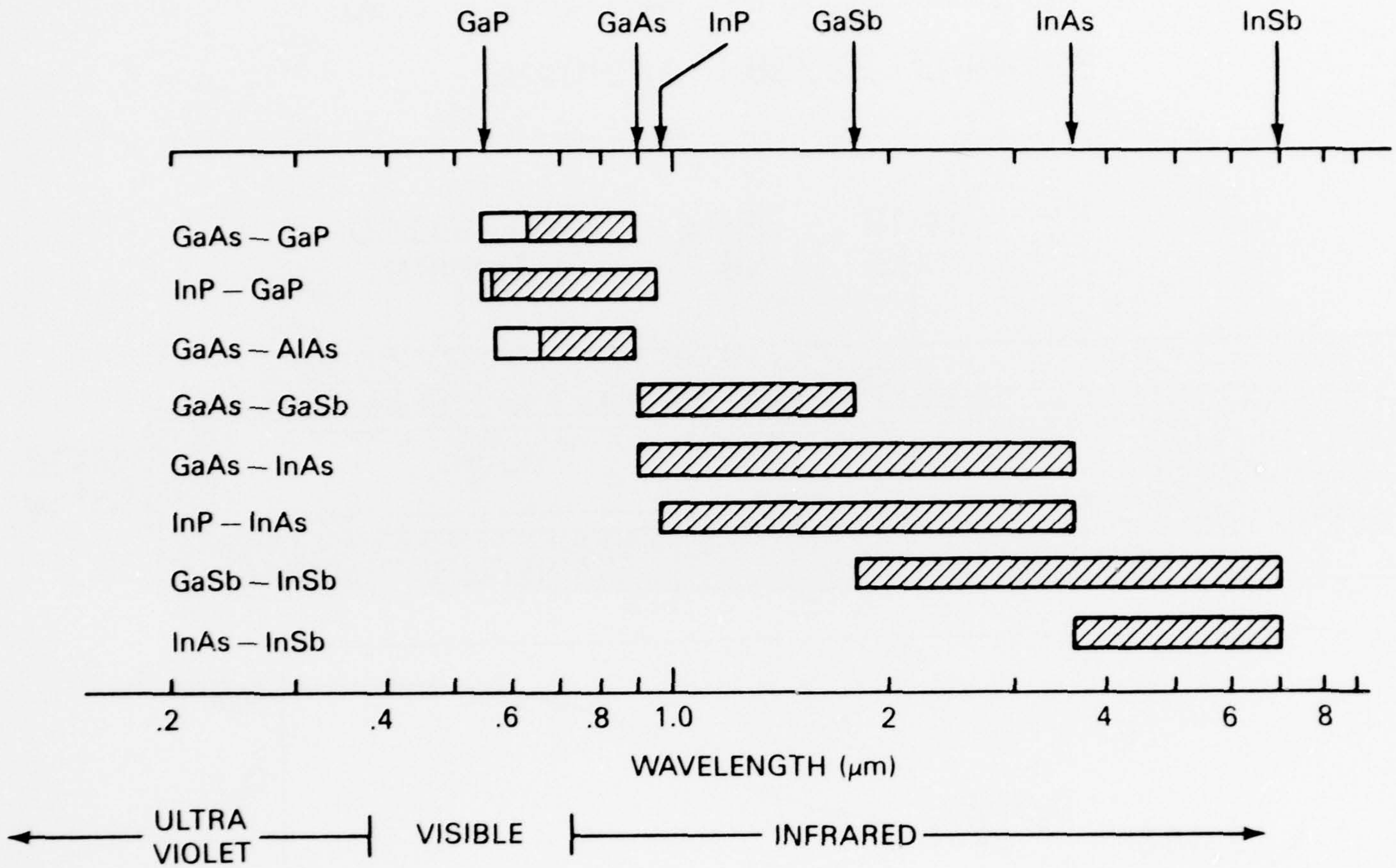
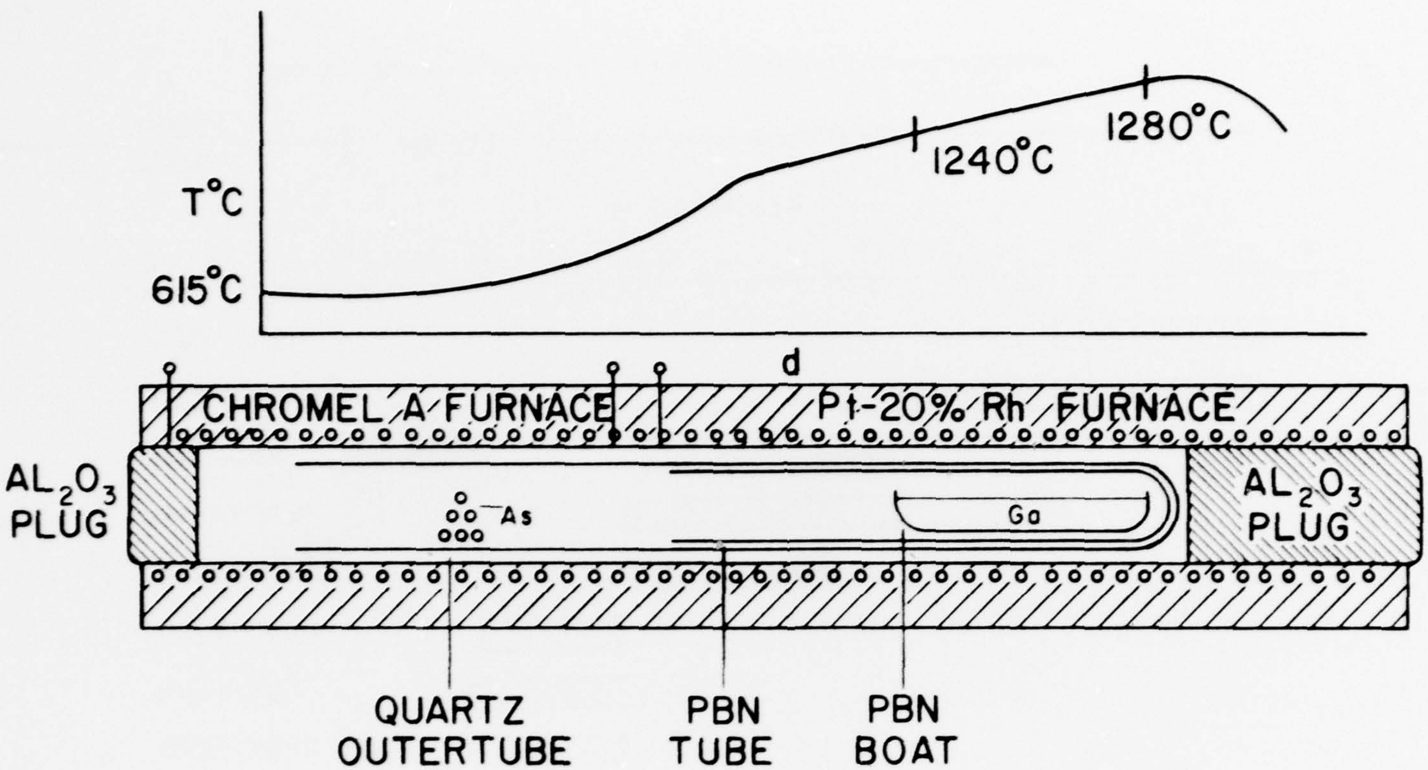



Fig. 2 — III—V alloys and the wavelength ranges (after C.J. Neusse)




GRADIENT FREEZE FURNACE

Fig. 3 — Furnace and typical profile for compounding GaAs

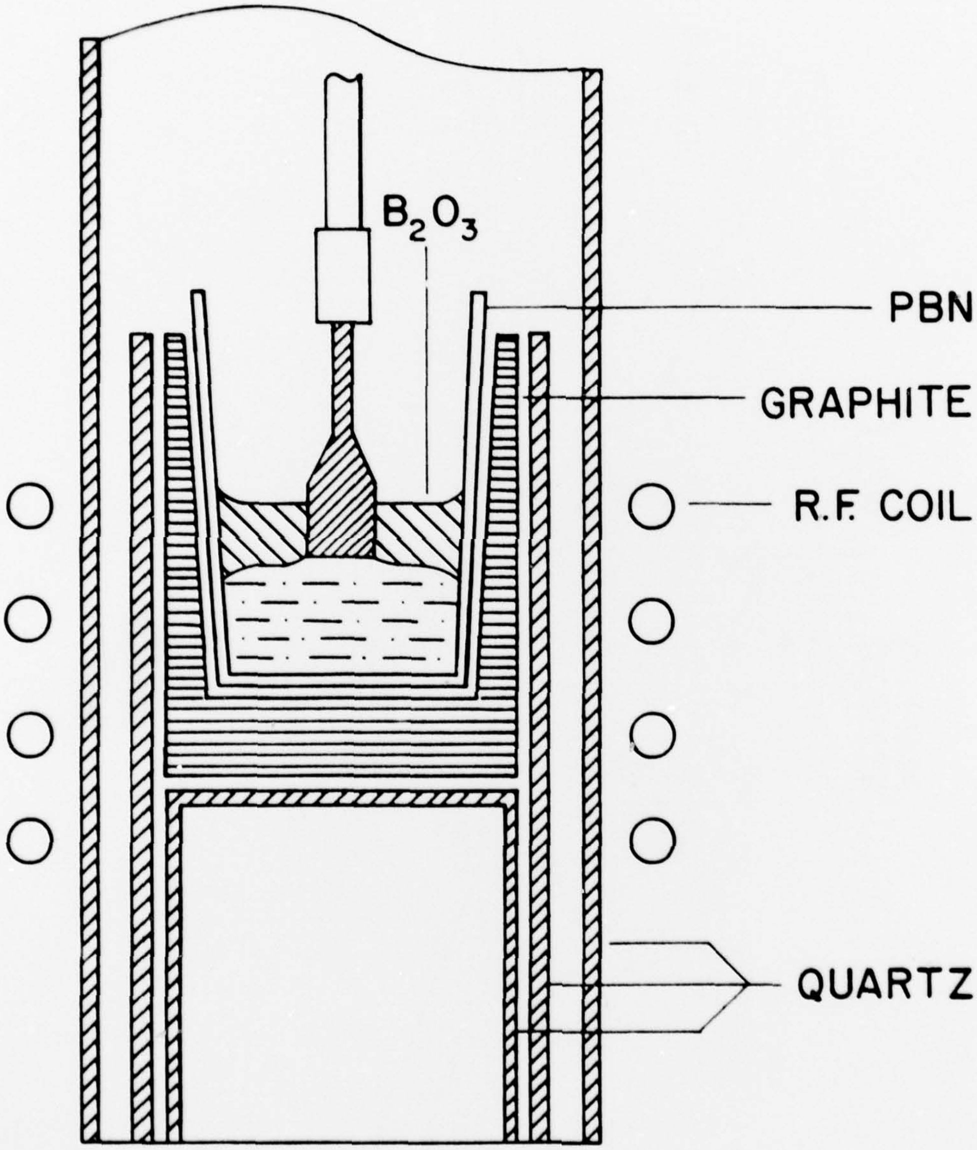



Fig. 4 — LEC furnace for single crystal growth

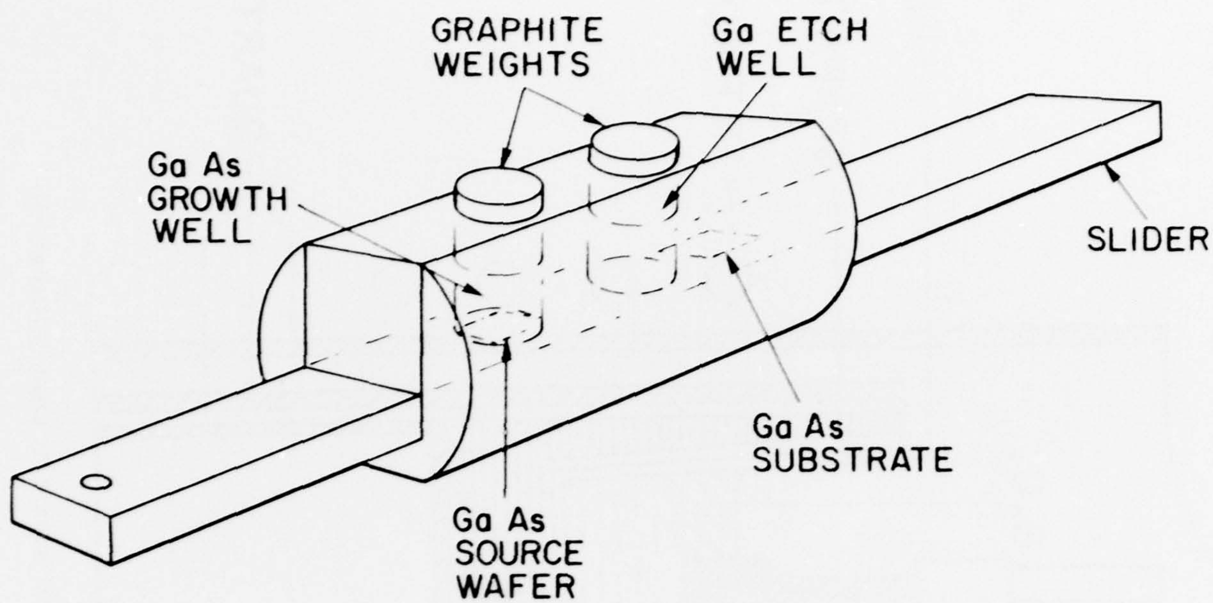



Fig. 5 — Epitaxial growth reactor

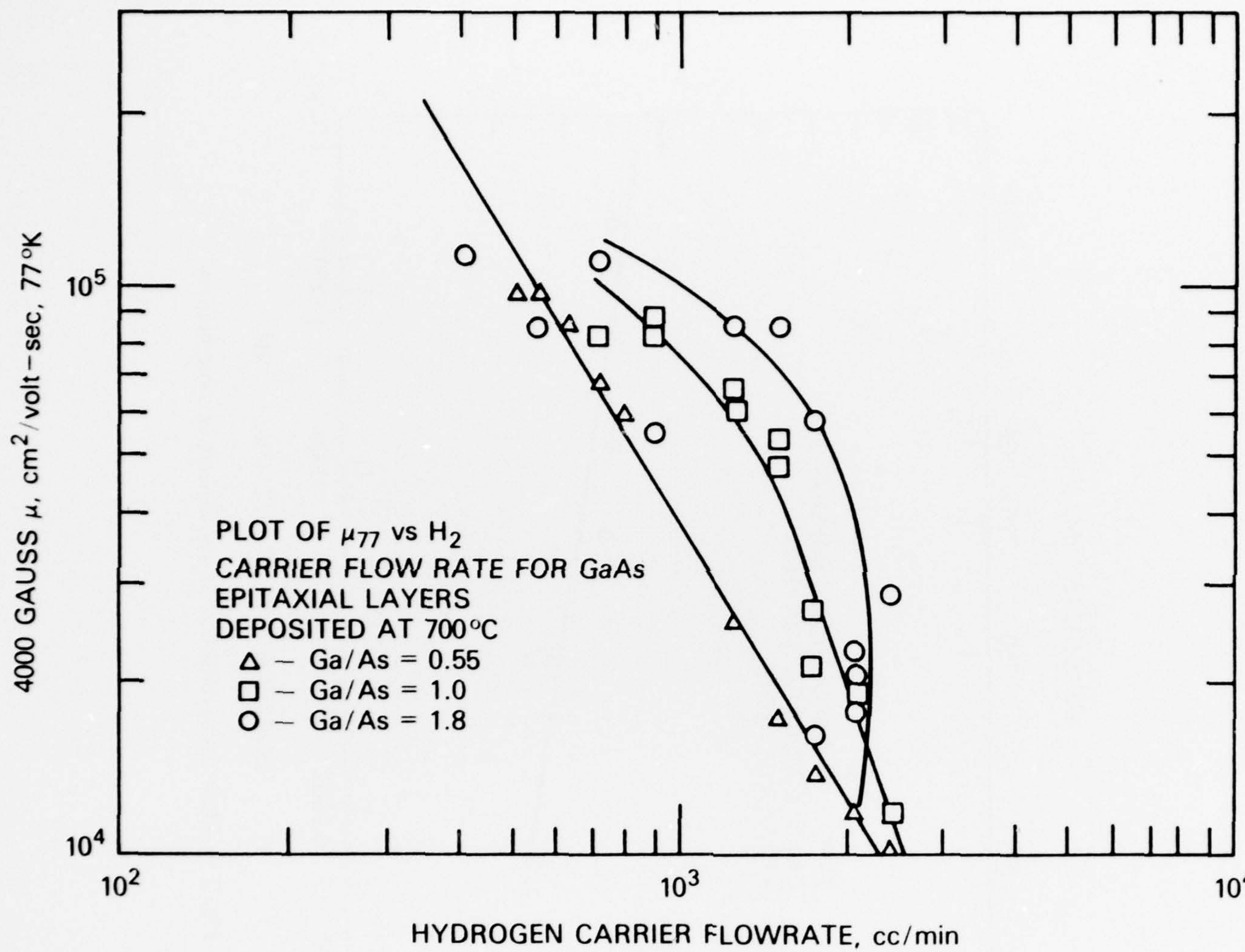



Fig. 6 — 4000 Gauss mobility versus the hydrogen flow rate

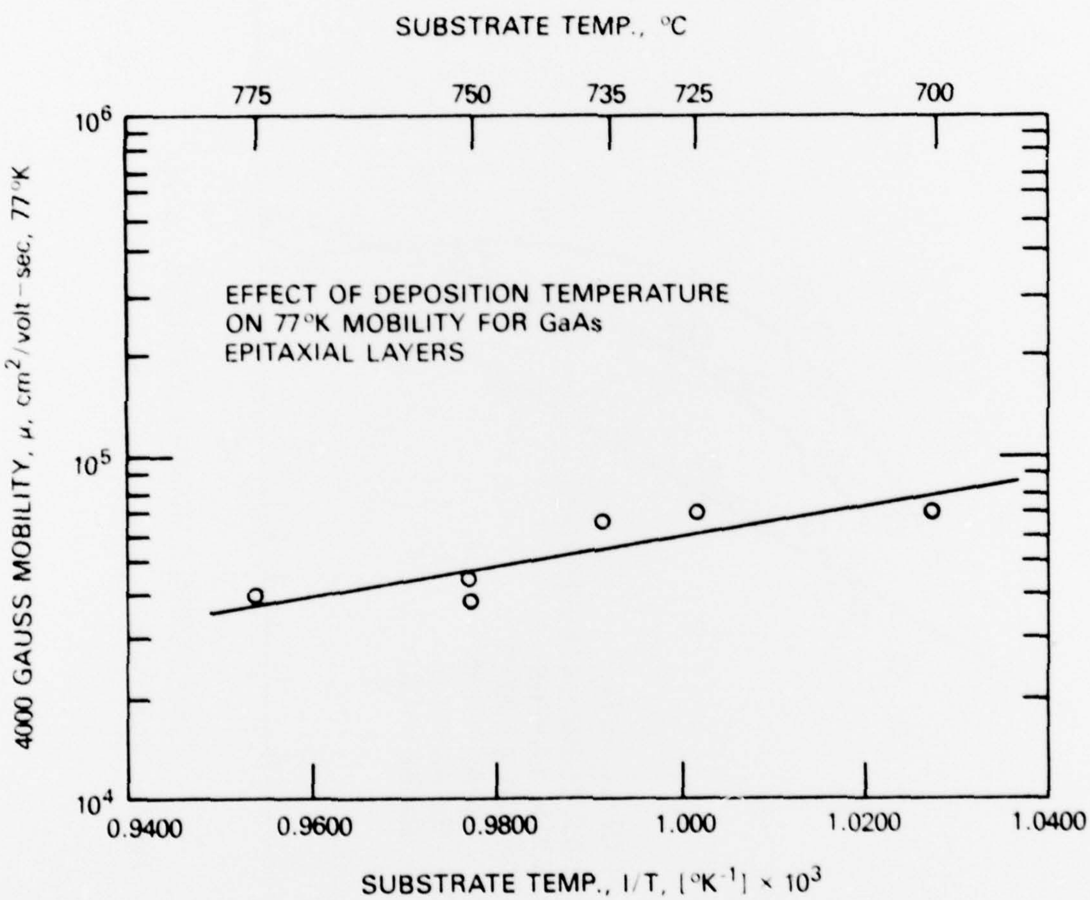



Fig. 7 — 4000 Gauss mobility versus deposition temperature

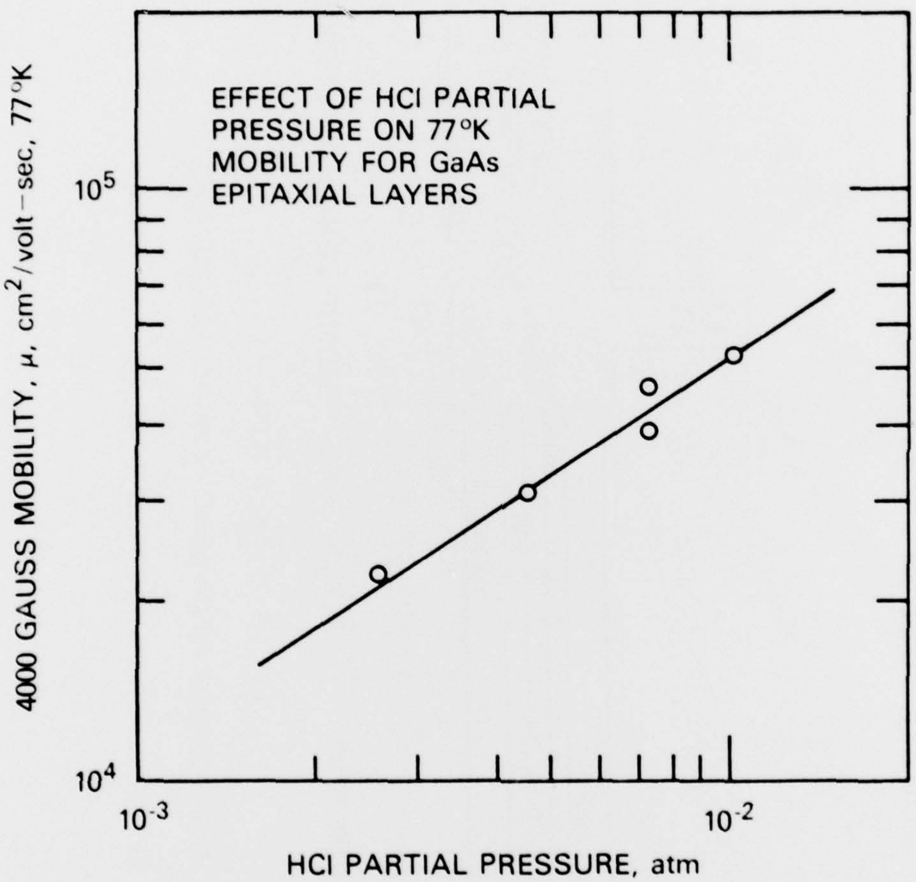



Fig. 8 — 4000 Gauss mobility versus HCℓ concentration

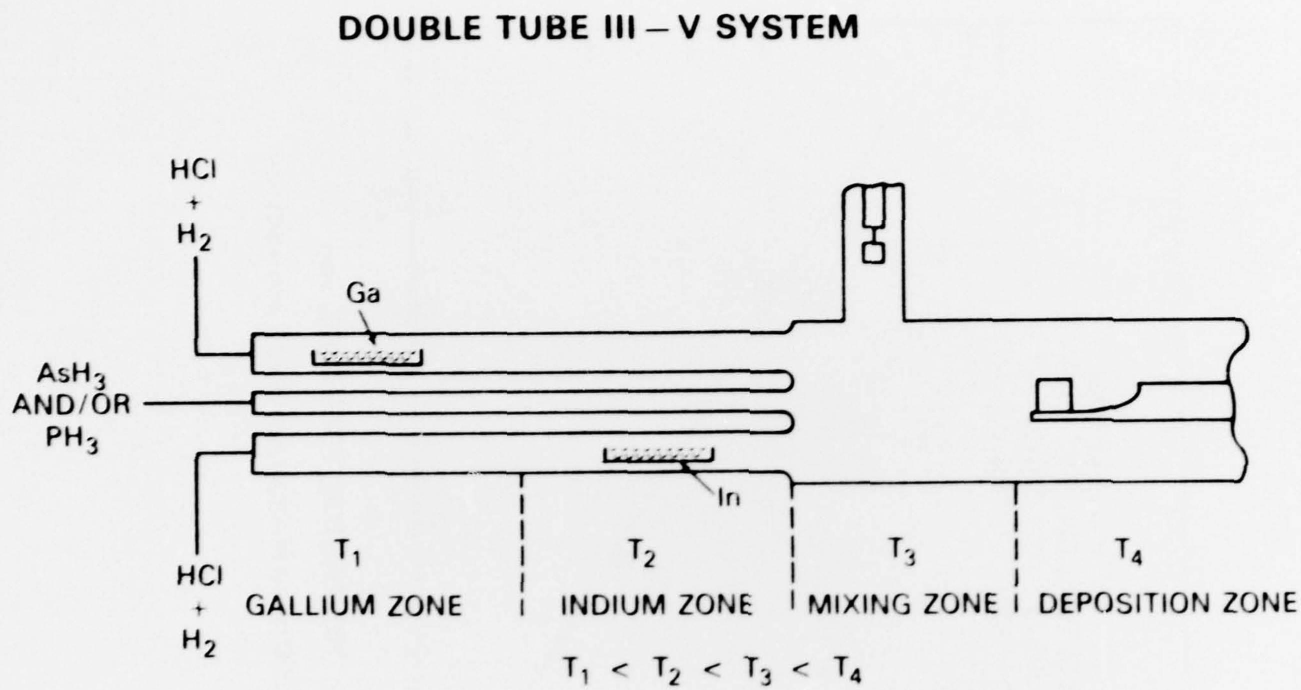



Fig. 9 — Epitaxial reactor for the growth of III–V quaternary alloys